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PHOSPHOR AND LIGHT-EMITTING DIODE

Field of the Invention

The present invention relates to phosphor and
5 light-emitting diode utilizing the same.

Description of Related Art

Following the introduction of blue light-emitting diode
(LED: light-emitting diode) in the year 1993, LEDs with the 3 primary
10 colors of light RGB (R: red, G: green, B: blue) have been made
available, and achieving white light by arranging these LEDs has
been suggested. However, since the emission outputs of the three
color LEDs are different, matching the characteristic of the
light-emitting diode of each color to achieve white light is
15 difficult. Even by concentrating the light-emitting diodes of
the three primary colors and arranging them on a same planar surface
such as when utilized as backlight for liquid crystal device, a
uniform white light source could not be achieved in the case of
visual verification at position near the light-emitting diodes.
20 Moreover, the color degrading rate of the light-emitting diode
of each color is different, and thus there is a problem in maintaining
long-term stability of the white light.

In order to solve these problems, an LED that combines
a blue LED chip and a YAG phosphor, which emits a yellow light
25 according to a blue light beam emitted from the blue LED chip,

was developed (see for example, reference 1: JP 2000-208815A).

Since white light can be obtained by using one type of LED, such LED is low in cost and has an excellent long-term stability of white light. Compared to light sources for conventional lighting

5 apparatus and the like, such white LED has the advantages such as long lifespan, high efficiency, high stability, low power consumption, and high response speed, and does not contain environmentally-unfriendly substance, and hence such kind of white LED is presently being utilized in liquid crystal device backlights of most mobile phones. Such white LED is expected to be utilized in lighting applications in future and to replace incandescent light bulb and fluorescent light as light source of the next generation.

The white LED disclosed in reference 1 has a structure in which a complex (coating member) composed of powder phosphor and resin is disposed over a light-emitting device that emits blue light. By irradiating a blue excitation light emitted from the light-emitting device onto the powder phosphor, a yellow fluorescence emitted from the phosphor is blended with the blue excitation light that passes through the resin, and the complex (coating member) composed of powder phosphor and resin emits a white light. However, in the case of long-term usage, the resin will gradually deteriorate and change color due to heat generated by the LED chip and the phosphor, or the light emitted therefrom, and this causes a decrease in emission intensity and lifespan of

the white light-emitting diode.

In addition, since the complex (coating member) composed of powder phosphor and resin is fixed to cover the LED chip, the thickness of the complex (coating member) composed of powder phosphor and resin tends to vary depending on the coating conditions of the resin, thus becoming the reason for color irregularities of the emitted light. Moreover, the white LED disclosed in reference 1 requires resin for fixing the phosphor and molding member made of resin, and has a complicated structure.

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Summary of the Invention

An object of the present invention is to provide a phosphor and a light-emitting diode that have a simple structure, excellent thermal resistance, light resistance and weather resistance, and can inhibit deterioration of emission intensity and shortening of lifespan of devices, such as light-emitting diode, caused by the conventional deterioration of resin.

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Another object of the present invention is to provide a phosphor and a light-emitting diode that can suppress color irregularities of emitted light.

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A phosphor of the present invention is composed of a single inorganic material, where when an excitation light composed of visible light is irradiated thereon, the phosphor emits a fluorescence of complimentary color with respect to a hue of the excitation light, and a portion of the excitation light transmits

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through the phosphor.

According to such structure, white light is emitted from the phosphor itself when an excitation light composed of visible light is irradiated on the phosphor, and thus the structure is simple with excellent thermal resistance, light resistance and weather resistance, and can inhibit deterioration of emission intensity and shortening of lifespan of devices, such as light-emitting diode, caused by conventional deterioration of resin. In other words, the phosphor emits a white light due to the blending of the excitation light transmitted through itself and the fluorescence. Further, the phosphor does not include resin, which is an organic material, and is composed of a single inorganic material with excellent thermal resistance, light resistance and weather resistance. In the case where such phosphor is utilized in devices such as light-emitting diode, since the devices are formed without using resin, coloration and deterioration of resin found in conventional light-emitting diode, due to heat generated by excitation light from the LED chip or the like and the phosphor itself, or light emitted therefrom, does not occur. As a result, the emission intensity of devices such as light-emitting diode is less prone to deterioration and lifespan of such devices become longer. Moreover, even in an ambient with severely high temperature, and even, for example, when the light-emitting diode is fixed to a housing vessel by inorganic adhesive such as metal for metallization, the light-emitting characteristic of the

light-emitting diode becomes less prone to change. Furthermore, even when exposed to ultraviolet from, for example, the sunlight, coloration and deterioration due to resin will not occur because no resin is included. And even in an ambient with severely high
5 temperature and high humidity for an extended period of time (2000 hours, 85°C temperature and 85% humidity), light-emitting characteristic of the light-emitting diode becomes less prone to change.

When the phosphor of the present invention has a panel
10 shape, the phosphor can be utilized as replacement material for complex composed of powder phosphor and resin in the conventional white light-emitting diode.

When the phosphor of the present invention is a panel with a large planar dimension, by installing a plurality of blue
15 LEDs on the lower surface of such panel, such phosphor can also be utilized as component for large surface light-emitting device having both light-emitting function and diffusing function.

Furthermore, by merely employing the phosphor of the present invention as a cover glass without fixing it onto a blue
20 light-emitting diode chip, the phosphor emits a white light and a white-light emitting diode with a simple structure can be achieved.

When the phosphor of the present invention has a panel shape, the thickness can be easily kept constant and a uniform
25 white light can be achieved. Moreover, since the balance of the

excitation light intensity and the fluorescence intensity can be varied freely by merely changing the thickness, white light with desirable chromaticity and color temperature can be achieved.

In the above described structure, it is preferable that
5 the wall thickness of the phosphor is between 0.1mm to 2mm so as to achieve a desirable white light with color temperature ranging from high to low. In the case where the wall thickness is thinner than 0.1mm, the fluorescence intensity with respect to the excitation light becomes small, the bluish hue becomes strong,
10 and a white light is difficult to be achieved. On the contrary, when the wall thickness is thicker than 2mm, the fluorescence intensity with respect to the excitation light becomes strong, the yellowish hue becomes strong, and a white light is difficult to be achieved. A more preferable wall thickness is between 0.1mm
15 to 1mm, and further more preferably between 0.3mm to 0.7mm.

White light is easily achieved when the excitation light composed of visible light is a light of which center wavelength is between 430nm to 490nm, and the fluorescence is a light of which center wavelength is between 530nm to 590nm, with regard to the
20 phosphor of the present invention.

When the phosphor of the present invention is composed of crystallized glass including Ce^{3+} and formed by precipitating garnet crystal, Ce^{3+} becomes the emission center, and the phosphor tends to absorb blue excitation light and emit yellow fluorescence
25 while allowing part of the blue excitation light to transmit through,

and thereby emits white light as the transmitted excitation light blends with the fluorescence.

Further, when the phosphor of the present invention is composed of crystallized glass formed by precipitating garnet crystal by subjecting an amorphous glass to thermal treatment, the garnet crystal disperses and remains within the matrix glass of the crystallized glass without including bubble. As a result, fluorescence and part of excitation light scatter in various directions while the phosphor itself acts as a scattering plate, and white light disperses in a wide angle. Moreover, since bubble does not exist, such as those found in complex composed of 2 or more different materials or in the interface of different materials, is present in the matrix glass or in the interface between the matrix glass and the precipitated crystal, fluorescence and excitation light that are not dispersed by the precipitated crystal are easily transmitted through, and thus increasing light-emitting efficiency.

Furthermore, when the phosphor of the present invention is composed of crystallized glass, the phosphor can be easily formed into arbitrary shapes, for example, panel shape, spherical shape, aspheric-lens shape, rod shape, cylindrical shape, fiber shape, and the like, and used according to applications.

Garnet crystal generally refers to crystals represented by $A_3B_2C_3O_{12}$ (A = Mg, Mn, Fe, Ca, Y, Gd, and the like; B = Al, Cr, Fe, Ga, Sc and the like; C = Al, Si, Ga, Ge and the like), and

the above described garnet crystal is preferably, in particular, YAG crystal ($\text{Y}_3\text{Al}_5\text{O}_{12}$ crystal) or YAG crystalline solid solution, so as to emit desirable yellow fluorescence. The YAG crystalline solid solution may be a YAG crystalline solid solution in which
5 a part of Y is replaced by at least one element selected from the group consisting of Gd, Sc, Ca and Mg, and/or a part of Al is replaced by at least one element selected from the group consisting of Ga, Si, Ge and Sc.

It is preferable that 0.01 to 5 mol% of Ce_2O_3 , which
10 serves as an emission center, is included. When the included amount of Ce_2O_3 is less than 0.01 mol%, it is difficult for the Ce_2O_3 to serve as a constituent of emission center, and the fluorescence intensity becomes insufficient. While when the included amount of Ce_2O_3 is more than 5 mol%, light-emitting efficiency will decrease
15 due to concentration quenching, and thus such included amount is not preferable. A preferable range for the included amount of Ce_2O_3 is between 0.01 to 4 mol%, and more preferably between 0.3 to 3 mol%.

The phosphor of the present invention is preferably
20 composed of a crystallized glass including 10 to 60 mol% of SiO_2 + B_2O_3 , 15 to 50 mol% of Al_2O_3 + GeO_2 + Ga_2O_3 , 5 to 30 mol% of Y_2O_3 + Gd_2O_3 , 0 to 25 mol% of Li_2O , 0 to 15 mol% of TiO_2 + ZrO_2 , and 0.01 to 5 mol% of Ce_2O_3 .

The phosphor of the present invention is more preferably
25 composed of a crystallized glass including 10 to 50 mol% of SiO_2 ,

15 to 45mol% of Al_2O_3 , 5 to 30mol% of Y_2O_3 , 0 to 15mol% of GeO_2 , 0 to 20mol% of Gd_2O_3 , 0 to 15mol% of Li_2O , 0 to 30mol% of CaO + MgO + Sc_2O_3 , and 0.01 to 5mol% of Ce_2O_3 .

Next, reasons for limiting the composition of the
5 crystallized glass of the present invention are set forth below.

SiO_2 and B_2O_3 are oxides for forming network of the glass, and are constituents that prevent devitrification during preparation of the mother glass, and the total included amount of SiO_2 and B_2O_3 is preferably between 10 to 60 mol%. When the
10 total amount of SiO_2 and B_2O_3 is less than 10 mol%, vitrification does not occur, and when the total included amount is more than 60 mol%, precipitation of desirable crystal becomes difficult. A preferable range for the total amount of SiO_2 and B_2O_3 is between 30 to 47 mol%. Included amount of SiO_2 is preferably between 10
15 to 50 mol%. When SiO_2 is less than 10 mol%, vitrification becomes difficult, and when SiO_2 is more than 50 mol%, precipitation of desirable crystal becomes difficult.

Al_2O_3 , Ga_2O_3 , GeO_2 are also constituents of garnet crystal and constituents that improve chemical resistance, and the total
20 included amount of Al_2O_3 , Ga_2O_3 , GeO_2 is preferably between 15 to 50 mol%. When the total included amount of Al_2O_3 , Ga_2O_3 , GeO_2 is less than 15 mol%, precipitation of garnet crystal becomes difficult and chemical resistance decreases. While when the total included amount is more than 50 mol%, vitrification and
25 precipitation of garnet crystal become difficult, and thus such

total included amount is not preferable. A preferable range for the total amount of Al_2O_3 , Ga_2O_3 , GeO_2 is between 20 to 40 mol%. Included amount of Al_2O_3 is preferably between 15 to 45 mol%. When the included amount of Al_2O_3 is less than 15 mol%, precipitation of garnet crystal becomes difficult and chemical resistance is prone to decrease. While when the included amount is more than 45 mol%, vitrification becomes difficult and different type of crystal is precipitated, and thus such included amount is not preferable. In addition, GeO_2 is partly soluble in garnet crystal and has an effect of increasing the crystal precipitation amount. The included amount of GeO_2 is preferably between 0 to 15 mol%.

Y_2O_3 and Gd_2O_3 are constituents of garnet crystal, as well as constituents that improve the uniform dispersion capability of Ce and prevent concentration quenching, and the total included amount of Y_2O_3 and Gd_2O_3 is preferably between 5 to 30 mol%. When the total included amount of Y_2O_3 and Gd_2O_3 is less than 5 mol%, precipitation of garnet crystal becomes difficult, while when the total included amount is more than 30 mol%, vitrification becomes difficult, and thus such total included amounts are not preferable. A preferable range for the total amount of Y_2O_3 and Gd_2O_3 is between 10 to 25 mol%. Included amount of Y_2O_3 is preferably between 5 to 30 mol%. When the included amount of Y_2O_3 is less than 5 mol%, precipitation of garnet crystal becomes difficult, while when the included amount is more than 30 mol%, vitrification becomes difficult and different type of crystal is precipitated, and thus

such included amounts are not preferable. In addition, Gd_2O_3 also has an effect of increasing the fluorescence wavelength into long wavelength and an effect of increasing the range of vitrification during the preparation of the mother glass. The included amount
5 of Gd_2O_3 is preferably between 0 to 20 mol%. When Gd_2O_3 is more than 20 mol%, precipitation of garnet crystal becomes difficult.

Li_2O is a constituent that serves as a network modifying compound and regulates the viscosity of the glass, without coarsening the crystal size and decreasing the precipitated crystal
10 amount, and the included amount of Li_2O is preferably between 0 to 25 mol%. When the included amount of Li_2O is more than 25 mol%, devitrification occurs in abundance during glass molding and vitrification becomes difficult, and such devitrification cannot be eliminated even by performing thermal treatment for
15 crystallization, and thus such included amount is not preferable. Specifically, when the included amount of Li_2O is more than 2 mol%, precipitation of garnet crystal becomes easy and thus such included amount is preferable. A preferable range for the included amount of Li_2O is between 2 to 16 mol%, and a more preferable range is
20 between 2.5 to 4.8 mol%. Further, when the included amount of Li_2O is less than 4 mol%, or when the included amount of Li_2O is more than or equal to 4 mol% while the total amount of SiO_2 and B_2O_3 is more than or equal to 40.5 mol%, completely no devitrification will be observed during glass molding and thus
25 such amount is more preferable. When the included amount of Li_2O

is more than 4 mol% and the total amount of SiO_2 and B_2O_3 is less than 40.5 mol%, slight devitrification will be observed during glass molding, but such devitrification will be eliminated by the thermal treatment for crystallization, and there is no particular
5 problem in the precipitation of dense garnet crystal.

The total amount of ZrO_2 and TiO_2 included can be up to 15 mol%, but garnet crystal is also precipitated without including ZrO_2 and TiO_2 . In actual fact, the lesser the total amount of ZrO_2 and TiO_2 , for example less than 3 mol%, and more preferably
10 including essentially no ZrO_2 and TiO_2 , the higher the light-emitting efficiency becomes and thus such total amount is preferable. When the total included amount of ZrO_2 and TiO_2 is more than 15 mol%, precipitation of desirable crystal becomes difficult and thus such total included amount is not preferable.
15 Here, "including essentially no ZrO_2 and TiO_2 " refers to the case where ZrO_2 and TiO_2 are completely not included, and also the case where the included amount of ZrO_2 and TiO_2 is a small amount of 0.1 mol% or less.

CaO , MgO and Sc_2O_3 are constituents that are solid soluble
20 in garnet crystal and can regulate the emission wavelength of Ce. The total amount of CaO , MgO and Sc_2O_3 included is preferably between 0 to 30 mol%, as devitrification occurs when the total amount thereof is more than 30 mol%.

Apart from the above described constituents, Na_2O , CaO ,
25 MgO , K_2O and the like can also be added independently or in

combination with a total amount of up to 15 mol%.

Further, since the light-emitting diode of the present invention is made by utilizing a phosphor with the above described structure, when excitation light composed of visible light is irradiated thereon, white light produced by the blending of the transmitted excitation light and the fluorescence is emitted. Moreover, since the phosphor is composed of a single inorganic material with excellent thermal resistance, light resistance and weather resistance, and does not include resin, which is an organic material, and also can be fixed without using resin, coloration and deterioration of resin found in conventional light-emitting diode, due to heat generated by excitation light from the LED chip or the like and the phosphor, or light emitted therefrom, does not occur. As a result, emission intensity is not prone to deterioration, long-term stability of the color of the white light is excellent, and lifespan increases.

In addition, since the crystallized glass of the present invention includes Ce^{3+} and is formed by precipitating garnet crystal, Ce^{3+} becomes the emission center, and the crystallized glass becomes a phosphor that absorbs blue excitation light and emits yellow fluorescence while allowing part of the blue excitation light to transmit through, and thereby emits white light as the transmitted excitation light blends with the fluorescence.

The crystallized glass of the present invention is formed by precipitating garnet crystal by subjecting an amorphous glass

to thermal treatment, and the garnet crystal disperses and remains within the matrix glass of the crystallized glass without including bubble. Therefore, when the crystallized glass of the present invention is utilized as a phosphor, fluorescence and part of
5 excitation light scatter in various directions while the phosphor itself acts as a scattering plate, and white light disperses in a wide angle. Moreover, since bubble does not exist, such as those found in complex composed of 2 or more different materials or in the interface of different materials, is present in the matrix
10 glass or in the interface between the matrix glass and the precipitated crystal, fluorescence and excitation light that are not dispersed by the precipitated crystal are easily transmitted through, and thus increasing light-emitting efficiency.

The crystallized glass of the present invention is melted
15 such that it becomes the above described composition, and crystallizable glass with arbitrary shapes, for example, panel shape, spherical shape, aspheric-lens shape, rod shape, cylindrical shape, fiber shape, and the like, can be fabricated by typical glass panel forming method such as roll forming, cutout
20 from casting, slot-down forming, overflow forming, down-draw forming, danner forming, and redraw forming. Thereafter, when the crystallizable glass is subjected to thermal treatment at between 1150 to 1600°C, and preferably between 1200 and 1500°C, for 0.5 to 20 hours, YAG crystal or YAG crystalline solid solution
25 can be precipitated and thus is preferable. In addition, the glass

may also be processed into desirable shapes after crystallization.

Brief Description of Drawings

FIG. 1 is a cross-sectional view representing a
5 light-emitting diode related to an embodiment.

FIG. 2 is a graph representing reflection fluorescence
spectra of example 1 and comparative example 1.

FIG. 3 is a graph representing transmitted light spectra
of example 1 and example 9.

10 FIG. 4 is a diagram representing chromaticity of
transmitted light when wall thickness is varied from 0.2mm to 1.0mm,
with regard to example 13.

Detailed Description of Preferred Embodiments

15 A light-emitting diode 20 related to an embodiment
includes, for example as illustrated in FIG. 1, a stem 3 including
a cathode lead terminal 1 and an anode lead terminal 2, a blue
light-emitting diode chip 4 connected to the anode lead terminal
2, a metal wire 5 connecting the cathode lead terminal 1 and the
20 blue light-emitting diode chip 4, a housing vessel 7 that is fixed
such that the stem 3 and the blue light-emitting diode chip are
air-tightly sealed, and of which a window portion 6 is formed above
the blue light-emitting diode chip, and a phosphor 8 attached to
the window portion 6 of the housing vessel 7. Therefore, the window
25 portion 6 not only functions as a cover glass but can also function

as a phosphor. In other words, a blue excitation light **9** emitted from the blue light-emitting diode chip **4** is irradiated on the phosphor **8**, and part of the excitation light **9** is absorbed by the phosphor **8**, which converts its wavelength, and a yellow fluorescence **9a** is emitted outward from the light-emitting diode **20**. In addition, part of the excitation light **9** also passes through the phosphor **8** and becomes a transmitted excitation light **9b**, which is then emitted outward from the light-emitting diode **20**. The yellow fluorescence **9a** and the blue transmitted excitation light **9b** blend to become a white light **10**.

Further, although the phosphor **8** is fixed to the metal housing vessel **7** by an adhesive **11**, the adhesive **11** does not deteriorate easily even if it is made of resin because the excitation light **9** does not come in direct contact with the adhesive **11**, and hence even if the phosphor **8** generates heat and the color of the adhesive **11** changes, the fluorescence **9a** and the transmitted excitation light **9b** will not be adversely affected. In the case where the adhesive **11** is composed of a glass with low melting point, even if the phosphor **8** generates heat, the adhesive **11** will not deteriorate, and thus it is preferable for the adhesive **11** to be composed of a glass with low melting point. Moreover, although the stem **3** and the housing vessel **7** can be air-tightly sealed by a sealant **12** composed of resin or glass with low melting point, deterioration of the sealant **12** decreases and reliability increases when the stem **3** and the housing vessel **7** are air-tightly sealed

by the sealant **12** composed, particularly, of glass with low melting point, and thus it is preferable for the sealant **12** to be composed, particularly, of glass with low melting point. In the case where the wall thickness of the phosphor **8** is between 0.1 to 2mm, excitation light can easily pass through and a desirable white light with color temperature ranging from high to low can be achieved, and thus such wall thickness is preferable. A preferable range for the wall thickness is between 0.2 to 1mm. Furthermore, it is preferable that the edges of the phosphor **8** are beveled to suppress chipping.

EXAMPLES

Hereinafter, the examples will be described.

Table 1 represents examples 1 to 8, table 2 represents examples 9 to 16, table 3 represents examples 17 to 24, and table 4 represents comparative examples 1 to 3 of the present invention. FIG. **2** is a graph representing the fluorescence spectra of the example 1 and a commercially available Ce:YAG phosphor (powder) when excitation light is reflected from sample surfaces. FIG. **3** is a graph representing the transmitted light spectra of examples 1 and 9 when excitation light is being transmitted. FIG. **4** is a diagram representing the chromaticity of transmitted light when wall thickness is varied from 0.2mm to 1.0mm, with regard to example 13.

Table 1

Mol%	Eg 1	Eg 2	Eg 3	Eg 4	Eg 5	Eg 6	Eg 7	Eg 8
SiO ₂	36.0	31.2	42.9	40.4	44.1	40.4	36.7	46.3
B ₂ O ₃	0.0	6.2	0.0	0.0	0.0	5.2	0.0	0.0
Al ₂ O ₃	30.9	17.8	22.1	19.4	22.6	15.3	34.0	28.4
Ga ₂ O ₃	0.0	12.2	0.0	0.0	0.0	7.3	0.0	0.0
Y ₂ O ₃	18.1	12.2	20.1	24.4	13.6	9.7	14.9	12.4
Gd ₂ O ₃	0.0	5.2	0.0	0.0	0.0	3.6	0.0	0.0
Li ₂ O	9.6	9.3	9.6	10.1	15.1	13.3	9.2	7.7
TiO ₂	3.0	3.2	3.0	3.2	2.5	0.0	2.8	2.8
ZrO ₂	1.9	2.2	1.9	2.0	1.7	4.8	1.9	1.9
Ce ₂ O ₃	0.5	0.5	0.4	0.5	0.4	0.4	0.5	0.5
Vitrification	△	△	○	△	○	○	△	○
Crystallization Temperature	1500°C	1400°C	1450°C	1450°C	1450°C	1450°C	1400°C	1400°C
Precipitated Crystal	YAG	YAG s.s.	YAG	YAG	YAG	YAG s.s.	YAG	YAG
Light-emitting Characteristic	○	○	○	○	○	○	○	○

*Eg = Example

Table 2

	Eg 9	Eg 10	Eg 11	Eg 12	Eg 13	Eg 14	Eg 15	Eg 16
SiO ₂	40.9	40.1	35.8	38.9	42.3	35.1	45.9	42.3
B ₂ O ₃	0.0	0.0	0.0	2.0	0.0	5.0	0.0	0.0
Al ₂ O ₃	35.0	34.3	30.7	35.0	34.2	34.3	23.6	34.2
Y ₂ O ₃	20.6	20.1	18.0	20.6	20.0	20.1	14.2	11.9
Gd ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.2
Li ₂ O	3.0	5.0	15.0	3.0	3.0	5.0	15.8	3.0
Ce ₂ O ₃	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Vitrification	○	△	△	○	○	△	○	○
Crystallization Temperature	1400°C	1450°C	1450°C	1400°C	1400°C	1450°C	1400°C	1380°C
Precipitated Crystal	YAG	YAG	YAG	YAG	YAG	YAG	YAG	YAG s.s.
Light-emitting Characteristic	○	○	○	○	○	○	○	○

5 *Eg = Example

Table 3

Mol%	Eg 17	Eg 18	Eg 19	Eg 20	Eg 21	Eg 22	Eg 23	Eg 24
SiO ₂	42.3	43.6	33.7	34.6	33.8	39.3	33.8	33.8
B ₂ O ₃	0.0	0.0	7.9	0.0	0.0	0.0	0.0	0.0
Al ₂ O ₃	34.2	29.7	34.6	35.5	35.7	34.2	33.7	33.7
GeO ₂	0.0	0.0	0.0	5.4	6.0	0.0	6.0	4.6
Y ₂ O ₃	7.8	23.1	20.3	20.8	12.4	20.0	10.4	10.4
Gd ₂ O ₃	12.2	0.0	0.0	0.0	8.5	0.0	8.5	8.5
Li ₂ O	3.0	3.1	3.0	3.1	3.1	3.0	3.1	3.1
CaO	0.0	0.0	0.0	0.0	0.0	3.0	2.0	1.4
MgO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0
Sc ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	2.0	2.0
Ce ₂ O ₃	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Vitrification	○	○	○	○	○	○	○	○
Crystallization Temperature	1380°C	1380°C	1380°C	1440°C	1430°C	1450°C	1450°C	1450°C
Precipitated Crystal	YAG s.s.	YAG	YAG	YAG	YAG s.s.	YAG	YAG s.s.	YAG s.s.
Light-emitting Characteristic	○	○	○	○	○	○	○	○

*Eg = Example

Table 4

	C.E 1	C.E 2	C.E 3
SiO ₂	58.0	36.0	38.9
B ₂ O ₃	4.3	0.0	2.0
Al ₂ O ₃	14.8	30.9	35.0
Ga ₂ O ₃	0.0	0.0	0.0
Y ₂ O ₃	12.2	18.1	20.6
Gd ₂ O ₃	0.0	0.0	0.0
Li ₂ O	7.5	9.6	3.0
TiO ₂	1.5	3.0	0.0
ZrO ₂	1.2	1.9	0.0
Ce ₂ O ₃	0.5	0.5	0.5
Vitrification	○	△	○
Crystallization Temperature	1400°C	-	-
Precipitated Crystal	Different Crystal	-	-
Light-emitting Characteristic	×	×	×

5 *C.E = Comparative Example

Crystallized glasses of the examples and the comparative examples were fabricated as follows.

First, glass raw materials, being prepared into compositions represented in Tables 1 to 4, were introduced into a platinum crucible and melted at 1650°C for 3 hours, and thereafter, crystallizable glasses were obtained by introducing the molten glass material onto a carbon panel. These crystalline glasses were then subjected to thermal treatment for 5 to 20 hours at the thermal treatment temperatures shown in Tables 1 to 4 to obtain the crystallized glasses of examples 1 to 24 and comparative example 1. With regard to examples 1, 2, 4, 7, 10, 11 and 14, although slight devitrification was observed during glass molding, such devitrification was eliminated by the thermal treatment for crystallization, and dense garnet crystals were precipitated. Comparative example 2 was the crystallizable glass of example 1 and comparative example 3 was the crystallizable glass of example 12, and both were not subjected to thermal treatment.

As shown in Tables 1 and 2, YAG crystals were precipitated in examples 1, 3-5, 7-15, 18-20 and 22, while YAG crystalline solid solutions were precipitated in examples 2, 6, 16, 17, 21, 23 and 24. Further, as shown in FIG. 2, a fluorescence spectrum (A) having a yellow fluorescence with a center wavelength that peaked at 540nm and a blue excitation light with a center wavelength that peaked at 460nm was detected in example 1 during reflection fluorescence spectrum determination. A white light emitting from a surface

opposite to the excitation light incidence plane of a panel sample was also observed with the unaided eye. Further, the reflection fluorescence intensity of example 1 was higher than the fluorescence intensity of a fluorescence spectrum (B) of a commercially available powder phosphor (P46-Y3 produced by Kasei Optonix, Ltd.) and displayed sufficient fluorescence intensity. Reflection fluorescence spectrum same as that of example 1 can also be achieved in examples 2 to 15. As shown in FIG. 3, a blue excitation light spectrum that peaked at 460nm, and a yellow fluorescence spectrum of which wavelength was converted and peaked at 540nm were observed in example 1 (C) and example 9 (D), and these spectrum intensities were high particularly in example 9 (D), in which no TiO_2 and ZrO_2 were included. With regard to example 13, after 1 hour of thermal treatment at 800°C, the emission intensity after thermal treatment was 95% or more with respect to the emission intensity before thermal treatment, thus displaying excellent thermal resistance. Moreover, with regard to example 13, the emission intensity after a 2000 hours treatment in an ambient with 85°C temperature and 85% humidity was 97% or more with respect to the emission intensity before such treatment, thus displaying excellent weather resistance.

As shown in FIG. 4, as the wall thickness of crystallized glass was varied from 0.2 to 1.0mm, and the chromaticity of the light that passed through such crystallized glass was measured with an integrating sphere and calculated by an analysis software,

a white light with a blue tinge (x value and y value were small) was emitted in the case where the wall thickness was thin, while a white light with a yellow tinge (x value and y value were large) was emitted as the wall thickness increased. Therefore, it was made known that desirable white light can be achieved by varying the wall thickness of crystallized glass.

On the other hand, with regard to comparative example 1, although vitrification occurred, the precipitated crystal was a different type of crystal (yttrium silicate) from YAG crystal, and hence the fluorescence intensity was low, and the center wavelength (450nm) of the fluorescence was in a wavelength region shorter than 540nm, and a yellow fluorescence could not be observed. Furthermore, comparative examples 2 and 3 included no YAG crystal and hence completely no fluorescence was emitted.

The precipitated crystal types were identified by powder X-ray diffractometry.

The reflection fluorescence characteristic (spectrum) was determined using a standard fluorescence spectrum measuring device, and by irradiating a light with 460nm excitation wavelength onto one side of a sample, and then detecting the light emitted from that side using a detector. With regard to the determination of fluorescence spectrum, example 1 utilized a fabricated crystallized glass panel processed to 20 X 20 X 0.5mm as the sample. In the case of commercially available powder phosphor, a pressed molded panel with 1mm of thickness was utilized as a measuring

sample.

The transmitted light spectrum was determined by irradiating a light with 460nm excitation wavelength onto one side of a sample, and then measuring the light emitted from the surface on the opposite side of said side using a standard fluorescence spectrum measuring device. The sample thickness was 0.4mm.

With regard to the vitrification in tables 1 to 3, "O" represents a homogeneous glass with no devitrification during molding were obtained, and "Δ" represents a slight devitrification during molding. Further, in tables 1 to 3, "YAG" represents that the precipitated crystal was YAG crystal, "YAG s.s." represents that the precipitated crystal was YAG crystalline solid solution, and "Different Crystal" represents types of crystal apart from YAG crystal and YAG crystalline solid solution. With regard to light-emitting characteristic, "O" represents the case where fluorescence spectrum with 530 to 590nm of center wavelength were achieved while "X" represents otherwise.

Possibility of Industrial Used

As described above, the phosphor of the present invention itself emits white light by combining with blue LED, particularly, when irradiated with excitation light composed of visible light, and hence has a simple structure with excellent thermal resistance, light resistance and weather resistance, and can inhibit deterioration of emission intensity and shortening of lifespan

of devices, such as light-emitting diode, caused by deterioration of resin. As a result, the phosphor of the present invention is suitable to be used as replacement material for complex (coating member) composed of powder phosphor and resin, in white
5 light-emitting diode utilized in backlights for lighting apparatuses, vehicles, display boards, liquid crystal devices and the like, or as component for large surface light-emitting device having both light emitting function and diffusing function.